行政院國家科學委員會專題研究計畫　期中進度報告

子計畫二:各種型態之奈米碳基材料開發及場發射元件之製作(2/3)

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計畫主持人：陳家富

計畫參與人員：林建良,徐振航,詹適宇,伍泰霖

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行政院國家科學委員會專題研究計畫期中報告

光資訊關鍵性材料製程與性質研究－子計畫二：各種型態之奈米碳基材料開發及場發射元件之製作(2/3)

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執行期限：92 年 8 月 1 日至 93 年 7 月 31 日

主持人：陳家富　　　　國立交通大學 材料科學與工程學系
計畫參與人員：林建良、徐振航、詹適宇、伍泰霖
國立交通大學 材料科學與工程學系

摘要

Material with high aspect ratio is essential for the typical field emission application. In this report, nano materials are synthesized and characterized using different techniques.

By using microwave plasma chemical vapor deposition system, Si nanotips are locally formed by an etching process. The microstructures of the Si tips are observed using both transmission electron microscopy and scanning electron microscopy. Further treatment is introduced to modify the tip structure to enhance the field emission properties comparative to the Si tips. With the similar technique, chromium carbide capped carbon nanotips are synthesized. This material also performs good uniformity and field emission properties. Proposed growth mechanism is demonstrate to provide a possible route to synthesized different catalyst cap on the tip in order to tune the field emission property.

Aluminum nitride nanotips are synthesized using thermal chemical vapor deposition. AlN nanotip appears in hexagonal shape and high resolution TEM shows a perfect crystalline structure. By controlling the cluster size and the growth temperature, the desired microstructure can be formed.

計畫緣由與目的

With the development of nanotechnology, nanostructures-structures that are defined as having at least one dimension between 1 and 100 nm have received steadily growing interest as a result of their peculiar and fascinating properties, and applications superior to their bulk counterparts. Many applications are predicted to involve with nanotechnology including optics, electronics, catalyst, ceramics, and storage media, etc. The most pertinent example is microelectronics, which “smaller” means greater performance ever since the invention of integrate circuits: more components per chip, faster operation, lower cost, and less power consumption.

Field emission from nano-sized material is one of the most important applications for the nanotechnology. The basic requirement of a nano emitter must have a high aspect ratio that field emission will take place. Among such an application, a revolution of the display technology come the field emission display. Compare with TFT-LCD flat panel display, field emission display has much more advantages such as high brightness, thin in dimension, wide view angle, low power consumption and a wide operating temperature. The mention advantages above make the field emission display a candidate for the new generation of the display technology.

Though the field emission technology has been developed over decades, a satisfied product has not yet been demonstrated. The key resolution of the current field emission display difficulties is the field emission efficiency and durability of the emitters. So far, carbon nanotubes have been extensively studied and tested for applications. It is not until now that precisely controlling the dimension and distribution of carbon nanotubes still a challenging issue. There’s still many materials which prohibit better performances than carbon nanotubes do.

In this project, various kinds of deposition methods are involved to synthesized nano-size materials. After the synthesis, instruments are incorporated to analysis and measure the character of the material. At the final stage, the material with desirable performance will be fabricated in to the device to achieve the practical applications.

結果與討論

A. Modification of Si Nano Emitters by Diamond - clad Process

The potential to achieve high-current devices is one of the most attractive issues of field emitters. In this work, needle-like Si tips with high aspect ratio is achieved by hydrogen plasma. Scanning electron microscopy (SEM) shows the average diameter and height of need-like Si tips are approximately 70 and 350 nm, respectively. To improve the field emission property of pure Si tips, the diamond-like carbon nanoparticles are further deposited on the top of the Si tips. Experimental results present that the diamond-like carbon-clad process improves the stability as well as the conductivity. Transmission electron microscopy (TEM) and Raman spectroscopy are used to observe their nanostructures and quality. Besides, the Auger electron spectrum also detects the partial growth of silicon carbide during modification process.

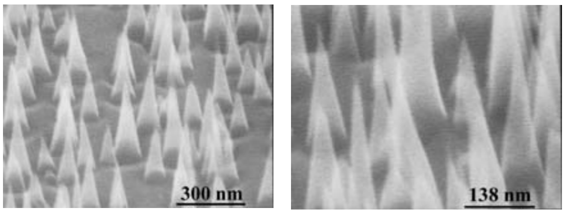

Fig. 1 (a) High and (b) low magnification of SEM photographs of Si nanotips

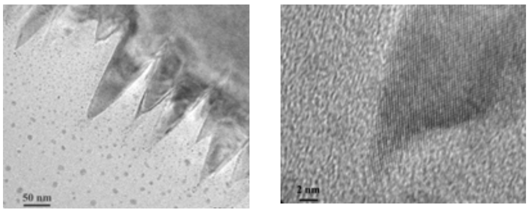

Fig. 2 TEM of (a) Si tips and (b) high-resolution images of individual Si tip.

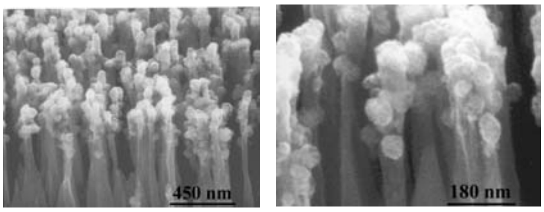

Fig. 3 (a) High and (b) low magnification of SEM photographs of DLC-clad Si nanotips

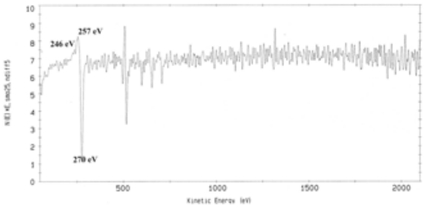

Fig. 4 AES profile of DLC-clad Si tips.

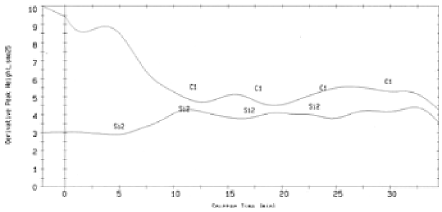

Fig. 5 AES surface survey of DLC-clad Si tips.

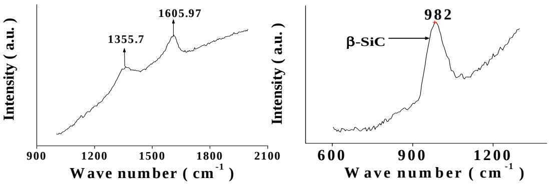

Fig. 6 Raman spectrum of DLC-clad Si nanotips.

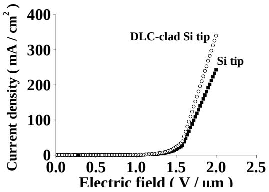

Fig. 7 Electric field (*E*) versus current density (*J*) of Si and DLC-clad Si tips, respectively.

According to the mentioned results, the major findings are summarized as follows:

1. The application of hydrogen plasma to induce Si tips is an easy method to produce high aspect ratio field emitters in many systems.
2. The average diameter and height of needle-like Si tips are approximately 70 and 350 nm, respectively.
3. Due to the competition between deposition and etching rate simultaneously occurred in the plasma, the needle-like shaped of Si

tips becomes blunt after DLC deposition.

4. Negative-bias effect is expected to enhance the growth rate of DLC during deposition.
5. Improvement on I-V characteristic of DLC-clad Si tips is due to the negative electron affinity (NEA) property and carbon nanoparticles.

B. Growth of chromium carbide capped-carbon nanotip using bias-assisted microwave plasma chemical vapor deposition

Chromium carbide capped-carbon nanotip was synthesized using bias-assisted microwave plasma chemical vapor deposition. Such a material grew up to about several hundreds of nanometer long and tens of nanometer in diameter. The applied bias is a significant parameter in the growth process that the higher bias is effective to increase the growth rate. However, the higher bias also contributes to a rapid formation of chromium carbide which leads to a shorter length of carbon nanotip at the same time. The higher ion energy also varies the tip diameter due to strong ion bombardment effect which is a competitor to deposition. It is found that the growth of chromium carbide capped-carbon nanotips reaches a limit due to the fully carburization of chromium.

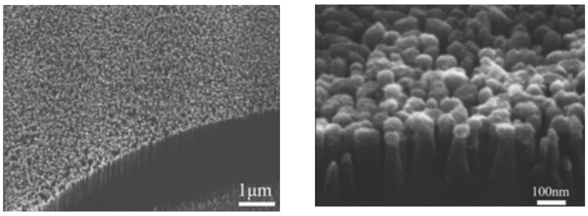

Fig. 1 (a) Low magnification SEM image showing the uniformity of the vertical aligned chromium carbide capped carbon nanotips. (b) SEM image of a close view.

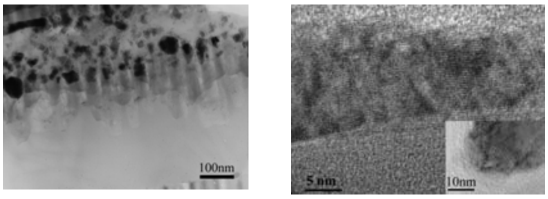

Fig. 2 TEM images showing (a) the cross-section view of chromium carbide capped carbon nanotips and, (b) high magnification view of an individual carbon nanotip and the inset shows the chromium carbide head.

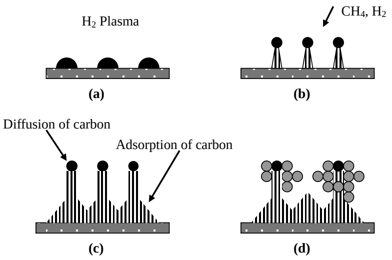

Fig. 3 Schematic diagram of proposed growth model (a) Formation of nucleation process; (b) cap growth; (c) deposition of carbon (d) asparagus-like structure forms.

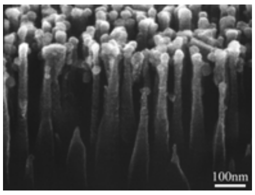

Fig. 4 Chromium carbide capped carbon nanotip grew under bias of -300 volt for 30 minutes

Chromium can be used as a catalyst to grow chromium carbide capped carbon nanotip with size of several tens of nanometers. Surface diffusion is believed to be the mechanism for the growth of carbon nanotip. The applied bias plays an important role that either assists the growth or etches the carbon away during growth. In other words, the dimension of the chromium carbide capped carbon nanotip can be controlled. And there exits length limit which is due to the fully carburization of chromium. By supplying sufficient bias, an asparagus–like structure forms.

C. Nucleation and growth of aluminum nitride nanotips using chemical vapor deposition

Hexagonal aluminium nitride nanotips (AlNNTs) have been fabricated on silicon (Si) substrates by simply using thermal chemical vapor deposition at temperatures of 950°C, using aluminium (Al) powders and ammonia gas. The initial growth of AlNNTs reveal that metal- silicide nanoclusters formed during early stages of growth served as the nucleation sites for the nanotips growth. Size control can be achieved by controlling the thickness of metal catalyst deposited on the silicon substrate. A stable and self-limited (001) facet often inhibits further growth of the AlNNTs grown at high temperatures. The area of the (001) facet increases with the increasing growth temperature. The structure and chemical composition of the AlNNTs were investigated by using XRD analysis, high-resolution electron microscopy, electron energy loss spectroscopy, and elemental mapping.

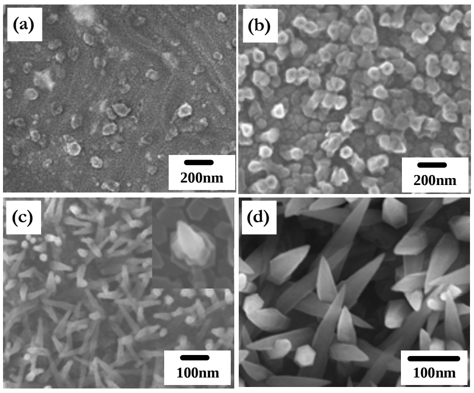

Fig.1. High resolution scanning electron microscope images of AlN nanotip grown for (a) 15 min, (b) 20 min, (c) 25 min, Inset shows the high magnificent of the initial growth of nanotip with crystalline nanoparticle on the base of the AlNNTs. (d) 30 min, respectively.

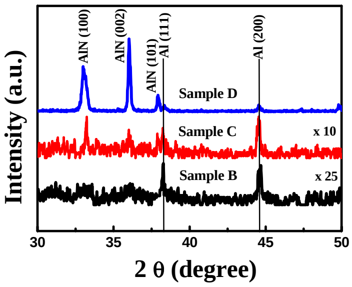

Fig.2. XRD spectra take from the sample B, C, and D, respectively.

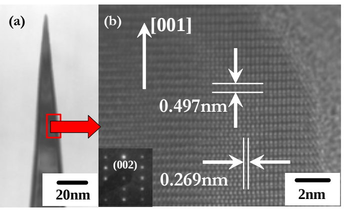

Fig. 3. (a) Low magnification HRTEM image and (b) atomic resolution TEM image of the h-AlN nanotip with growth direction of [001] with [110] zone axis. Inset in (b) shows SAED image of the AlN nanotips.

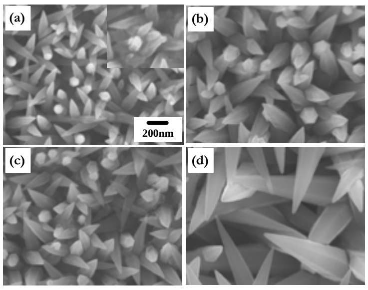

Fig.4. HR-SEM images of AlN nanotips grown with (a) Au (15nm), (b) Al (15nm), (c) Pt(15nm), (d) Pt (60nm) coating on the Si substrate, respectively.

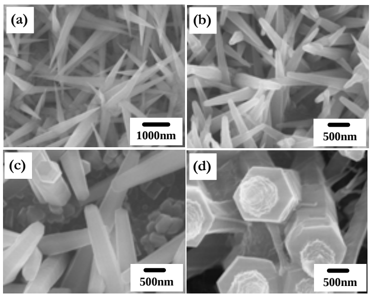

Fig.5. HR-SEM images of AlN nanotips on silicon substrates coated with 15 nm of gold grown under (a) 950℃, (b) 1000℃, (c) 1100℃, (d) 1200℃, respectively.

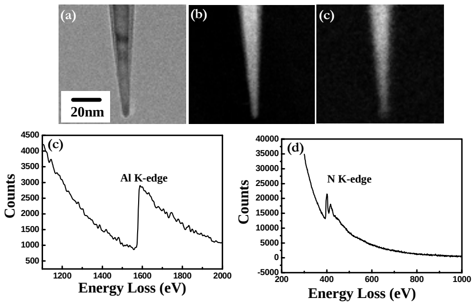

Fig. 6. EELS experiments and elemental mapping of the AlN nanotips: (a) Original TEM image; (b) Al mapping; (c) N mapping. Corresponding EELS spectra exhibiting (d) Al K-edge at 1560 eV, (e) N K-edge at 401eV. All the EELS analysis were obtained from AlN nanotip(s) prepared on 15 nm Au coated Si substrate at 950℃ for 30 minutes.

In summary, the growth of highly pure and high density hexagonal aluminum nitride nanotips on silicon substrates via a thermal chemical vapor deposition system has been demonstrated. The AlNNTs grow by vapour-solid mechanism and their preferred growth direction (long axis) is [001]. Composition and structures of the AlNNTs have been confirmed by XRD, HRTEM, SAED, and EELS. Optimal conditions for the growth of these nanotips are 950℃ growth temperature and 30 minutes growth time under flowing NH_3 with Au as catalyst. The morphology of the nanotips is determined by the size of the metal or metal silicide phase nanoparticulates formed during the initial stages of growth. It is believed that this nanotip structure have potential applications as field emission tips, and other nanoscale heterojunction devices.

計畫成果自評

本計畫成功的利用多種方法合成各種型態的奈米材料, 包括奈米碳管、奈米矽尖錐、奈米碳尖錐及奈米氮化鋁尖錐。

在直接利用矽晶圓的情況下，藉由偏壓輔助微波電漿化學氣相沈積法，可蝕刻形成矽的奈米尖錐，更可再藉由後處理披覆類鑽薄膜以增進其場發射性質。此法可望直接利用現有半導體製程以製作元件。另外直接利用觸媒成長法選擇性成長奈米碳尖錐及奈米氮化鋁尖錐，皆具有優良的性質。並深入研究其成長特性進而控制奈米材料的外型及組成。

除了可以直接應用於場發射元件上，這些一維的奈米材料因具有極高的表面積，可應用在需高表面積反應的需求上，例如燃料電池、氣體偵測器及生化感測器上。除此之外，這些奈米材料仍待更進一步的開發與應用。